CD221. LECTURE 11. STATISTICAL THERMODYNAMICS IN THE CANONICAL FORMALISM

Our earlier calculations have shown that for a system at constant temperature (and fixed volume and number of particles), the probability p_α that it can be found in one of its accessible microstates α is given by the expression

$$p_\alpha = \frac{e^{-\beta U_\alpha}}{Q} \tag{1}$$

where U_α is the energy the system has in the microstate α, and Q, the so-called canonical partition function, is defined as $Q = \sum_\alpha e^{-\beta U_\alpha}$. What is the connection between this expression and the system's macroscopic properties?

To find this connection, we expect that it might be useful to first look for a way to calculate the entropy of the system S, since we already know how to relate entropy to the number of microstates. But when the system is in a definite microstate (say, α), S is 0 (since there's only one such state.) On the other hand, the entropy of the *reservoir* when the system is in α, which we will denote $S_{R\alpha}$, is non-zero – it is given by $S_{R\alpha} = k_B \ln \Omega_{R\alpha}$, with $\Omega_{R\alpha}$ being the number of microstates of the reservoir when the system is in α. At the same time, because the system is in contact with a thermal reservoir, it does not remain indefinitely in α, but constantly moves into and out of other states as energy is exchanged between the two sub-systems. In the process, the number of microstates accessible to the reservoir constantly changes too, and so, therefore, does its entropy, which now depends on which of the microstates the system happens to be in. These microstates aren't equally likely, but occur with the probability p_α given by Eq. (1), so over long time scales, as the system settles into equilibrium, the entropy of the reservoir assumes an *average* value $\overline{S}_R$, which can be defined as

$$\overline{S}_R = \sum_\alpha p_\alpha S_{R\alpha} \tag{2}$$

The entropy of the composite system as a whole (reservoir + system of interest) remains unchanged throughout, and has some value that we'll denote S_0. Since entropy is additive, if the reservoir entropy is $\overline{S}_R$, we can regard the entropy S of the system as

$$S = S_0 - \overline{S}_R \tag{3}$$

We can now express S in terms of p_α by introducing the Boltzmann equation into Eq. (3), following these steps:

$$S = S_0 - \sum_\alpha p_\alpha S_{R\alpha}$$

$$= k_B \ln \Omega_0 - k_B \sum_\alpha p_\alpha \ln \Omega_{R\alpha}$$

$$= k_B \ln \Omega_0 - k_B \sum_\alpha p_\alpha (\ln \Omega_{R\alpha} - \ln \Omega_0 + \ln \Omega_0)$$

$$= k_B \ln \Omega_0 - k_B \sum_\alpha p_\alpha \ln \frac{\Omega_{R\alpha}}{\Omega_0} - k_B \sum_\alpha p_\alpha \ln \Omega_0$$

$$= k_B \ln \Omega_0 - k_B \sum_\alpha p_\alpha \ln p_\alpha - k_B \ln \Omega_0 \sum_\alpha p_\alpha$$

$$= -k_B \sum_\alpha p_\alpha \ln p_\alpha \tag{4}$$

where in going from the last-but-one to the last step, we have made use of the normalization condition $\sum_\alpha p_\alpha = 1$.

If Eq. (4) is indeed the correct definition of the entropy S of the system, it must be applicable even to a system that is completely closed (in other words, to a system of fixed energy that is isolated from its surroundings.) For such a system, $p_\alpha = 1/\Omega$ (by the assumption of equal à priori probabilities), and if this result is substituted into Eq. (4), the equation reduces to

$$S = -k_B \sum_\alpha \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) = k_B \frac{1}{\Omega} \ln \Omega \sum_\alpha = k_B \ln \Omega \tag{5}$$

after recognizing that $\sum_\alpha = \Omega$. Since Eq. (5) is the correct expression for the entropy of a system in isolation, Eq. (4) can be assumed to be the correct expression for the entropy of a system in contact with a thermal reservoir.

If p_α in Eq. (4) is now replaced by the expression given in Eq. (1), we have the following:

$$S = -k_B \sum_\alpha p_\alpha \ln \left(\frac{e^{-\beta U_\alpha}}{Q} \right)$$

$$= -k_B \sum_\alpha p_\alpha \left(-\beta U_\alpha - \ln Q \right)$$

$$= k_B \left(\beta \sum_\alpha p_\alpha U_\alpha + \ln Q \sum_\alpha p_\alpha \right)$$

$$= \frac{\overline{U}}{T} + k_B \ln Q \tag{6}$$

where in the last step we have introduced the definition of the average energy as $\overline{U} = \sum_\alpha p_\alpha U_\alpha$. $\overline{U}$ is the quantity that we would obtain in a thermodynamic measurement of the system's energy. It is therefore also the quantity that we have so far denoted U.

Equation (6) can be rearranged to

$$U - TS = -k_B T \ln Q \tag{7}$$

But the LHS of this equation is just the definition of the Helmholtz potential F, and so

$$\boxed{F = -k_B T \ln Q} \tag{8}$$

Because Q depends on V and N (through U_α, which depends on these quantities), F also depends on T, V and N, i.e., $F = F(T, V, N)$. So by calculating Q (by carrying out the sum $\sum_\alpha e^{-\beta U_\alpha}$) we can determine a system's fundamental relation.

Equation (8) is the key equation of the canonical formalism. We'll see later how it can be used to derive thermodynamic information about real systems. In the meantime, we'll see how the properties of systems characterized by other sets of macroscopic variables – T, V and μ to begin with, and then T, P and N – can be related to their various microstates.

• Systems in Contact with Thermal and Particle Reservoirs

When the state of a system is characterized macroscopically by other intensive variables besides T, what is the connection now – if any – between the system's microstates and its bulk properties? Suppose, for instance, that the system is contact with both a thermal and a particle reservoir, as in the figure below, so that its temperature T *and* chemical potential μ are constant: what can we then say about the thermodynamics of this system if we know how its atoms or molecules behave at the microscopic level? (The present discussion closely follows the discussion of the previous section.)

U_0, V_0, N_0

Temperature and particle reservoir

System

T, V, μ
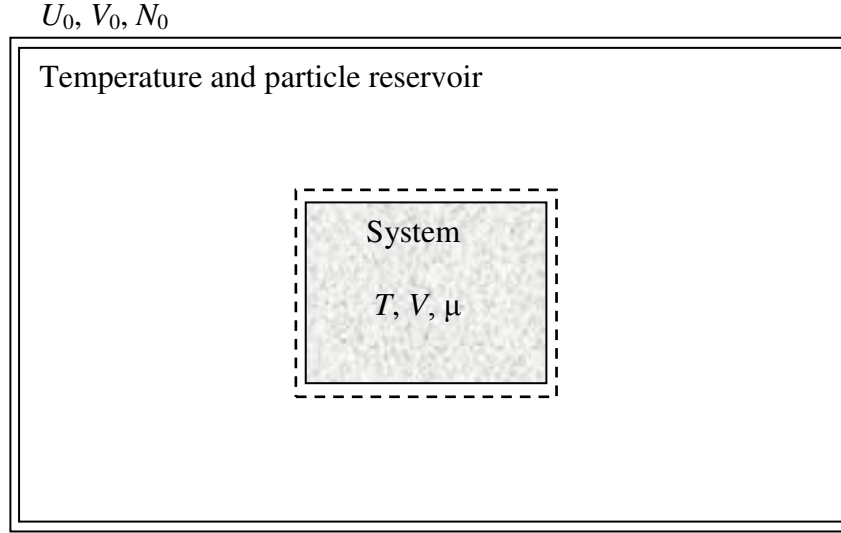
To begin with, let's assume that system and reservoir together constitute a closed composite system of total energy U_0, total volume V_0 and total number of particles N_0. Because the boundary of the system is diathermal and permeable, energy and matter flow into and out of the system, maintaining its temperature at T and chemical potential at μ. In the process, however, the energy U and particle number N of the system fluctuate in time, as depicted schematically below. Over the long timescales characteristic of thermodynamic measurements, however, these fluctuations average out to produce a time-independent energy $\overline{U}$ and a time-independent particle number $\overline{N}$.
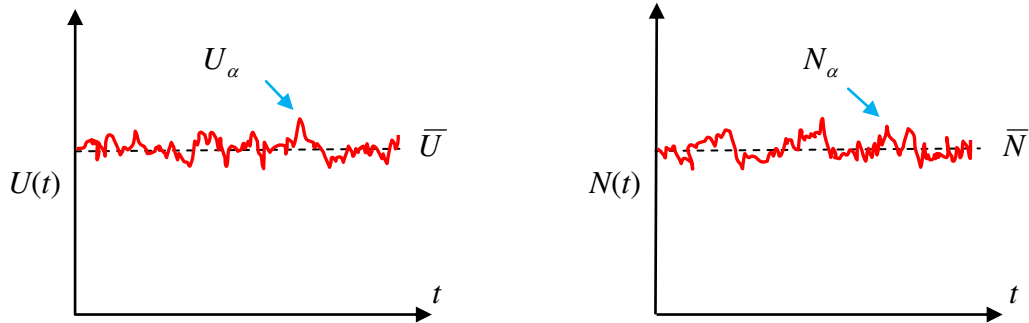
At any one instant of time, the system will be in one of the microstates α that is compatible with the system having the energy and particle number values that characterize it at that particular instant. Let these values be U_α and N_α. As these values change, so do those of the reservoir, but subject to the constraint that the energy and particle number of the composite system as a whole remain fixed at U_0 and N_0. When

the system is in α, let the energy and particle number of the reservoir be $U_{R\alpha}$ and $N_{R\alpha}$, with $U_{R\alpha} \gg U_\alpha$ and $N_{R\alpha} \gg N_\alpha$. From the fact that the composite system is closed,

$$U_{R\alpha} = U_0 - U_\alpha \tag{9a}$$

and

$$N_{R\alpha} = N_0 - N_\alpha \tag{9b}$$

In general, there will be a large number of microstates of the reservoir, $\Omega_{R\alpha}$, with these values, and this number will depend on $U_{R\alpha}$ and $N_{R\alpha}$. That is,

$$\Omega_{R\alpha} = \Omega_R(U_{R\alpha}, N_{R\alpha})$$

$$= \Omega_R(U_0 - U_\alpha, N_0 - N_\alpha) \tag{10}$$

(The volume dependence is not shown explicitly because V is kept fixed at all times.)

When the system is in α, the number of microstates of the *composite system*, call it $\Omega_{0\alpha}$, is the product of the corresponding number of reservoir and system microstates. In other words,

$$\Omega_{0\alpha} = \Omega_{R\alpha} \times 1 = \Omega_{R\alpha} \tag{11}$$

(The factor of 1 in this equation reflects the fact that there is just a single microstate α.) The *total* number of microstates of the composite system, Ω_0 (with energy U_0 and particle number N_0) is much larger. Of these Ω_0 microstates of the composite system (all equally likely), $\Omega_{0\alpha}$ ($= \Omega_{R\alpha}$) of them correspond to the system being in microstate α. So the probability of the system finding itself in α (call it p_α) is the number of ways this can happen ($\Omega_{R\alpha}$) divided by the number of ways anything can happen (Ω_0). That is,

$$p_\alpha = \frac{\Omega_{R\alpha}}{\Omega_0} \tag{12}$$

From the Boltzmann equation,

$$\Omega_{R\alpha} = \exp(S_{R\alpha}/k_B) \tag{13}$$

where

$$S_{R\alpha} = S_R(U_{R\alpha}, N_{N\alpha})$$

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$$= S_R(U_0 - U_\alpha, N_0 - N_\alpha)$$

$$\approx S_R(U_0, N_0) - \frac{\partial S_R}{\partial U_R} U_\alpha - \frac{\partial S_R}{\partial N_R} N_\alpha + \cdots \tag{14}$$

From thermodynamics, we have the general relations $\partial S / \partial U = 1/T$ and $\partial S / \partial N = -\mu / T$, and so Eq. (14) becomes

$$S_R = S_R(U_0, N_0) - \frac{U_\alpha}{T} + \frac{\mu N_\alpha}{T} \tag{15}$$

Substituting Eq. (15) into the expression for the probability p_α [Eq. (12)], we arrive at

$$p_\alpha = \frac{1}{\Omega_0} e^{S_R(U_0, N_0)/k_B} e^{-\beta U_\alpha + \beta \mu N_\alpha}$$

$$= \frac{1}{\Xi} e^{-\beta U_\alpha + \beta \mu N_\alpha} \tag{16}$$

where Ξ is a constant and $\beta \equiv 1/k_B T$. We can find an expression for this constant by requiring that p_α be normalized, i.e., by imposing the condition $\sum_\alpha p_\alpha = 1$. This condition leads to

$$\Xi = \sum_\alpha e^{-\beta U_\alpha + \beta \mu N_\alpha} \tag{17}$$

The quantity Ξ is known as the <u>grand canonical partition function</u>, and from its definition, it's clear that it is a function of T, V and μ. That is,

$$\Xi = \Xi(T, V, \mu) \tag{18}$$

Furthermore, from Eq. (16) we see again that when a system is not isolated but instead interacts with its surroundings (in the present case through contact with energy and particle reservoirs), the probability of its being in a particular microstate is not uniform but depends on how much energy and how many particles the microstate contains.

It remains now to connect Ξ to the thermodynamics of the system. We can do this in the same way we had connected Q to F, by calculating the entropy of the system using Eq. (4) (which is quite general), but with p_α in that equation now substituted by Eq. (16). This leads to

$$S = -k_B \sum_\alpha p_\alpha \ln \frac{1}{\Xi} e^{-\beta U_\alpha + \beta \mu N_\alpha}$$

$$= -k_B \sum_\alpha p_\alpha \left[-\beta U_\alpha + \beta \mu N_\alpha - \ln \Xi \right]$$

$$= \frac{\overline{U}}{T} - \frac{\mu \overline{N}}{T} + k_B \ln \Xi \tag{19}$$

where $\overline{U}$ and $\overline{N}$ are averages defined as $\overline{U} = \sum_\alpha p_\alpha U_\alpha$ and $\overline{N} = \sum_\alpha p_\alpha N_\alpha$. They are exactly the same thermodynamic quantities we have so far been denoting U and N and that we will now continue to refer to by these symbols. (But they must be understood as actually corresponding to quantities that are the result of the averaging process implicit in the nature of a thermodynamic measurement.)

After multiplying Eq. (19) by T and rearranging, we arrive at

$$U - TS - \mu N = -k_B T \ln \Xi \tag{20}$$

You should recognize the left hand side of this equation as the definition of the Legendre transform of U with respect to S and N, and this Legendre transform is the thermodynamic potential Ψ, the grand potential. So finally,

$$\Psi = -k_B T \ln \Xi. \tag{21}$$

Because Ξ is a function of T, V and μ, the calculation of Ξ by the sum over states in Eq. (17), leads, through Eq. (21), to the fundamental equation $\Psi = \Psi(T, V, \mu)$, and from there to all the thermodynamic properties of the system.

• <u>More General Macroscopic Constraints</u>

At this point, it should start becoming clear that depending on the variables used to specify the macroscopic state of a system, we will find that the connection between the microstates of the system and its thermodynamics is expressed by a relation analogous to Eq. (21), a relation, in other words, between a thermodynamic potential and the logarithm of a suitably defined partition function. Consider, for instance, a system specified macroscopically by the variables T, P and N. For such a system to be at constant T and P (at fixed N) it must be in contact with a thermal and pressure reservoir. This means that it can exchange energy and volume (not particles) with the reservoir. So at different instants of time, as the system moves from one microstate to another, its energy and volume fluctuate, and if these variables have the values U_α and V_α in the state α, you should be

able to show, following the same steps as above, that the probability p_α of finding the system in α is

$$p_\alpha = \frac{1}{\Delta} e^{-\beta(U_\alpha + PV_\alpha)} \qquad (22)$$

where Δ, the so-called <u>isothermal-isobaric partition function</u>, is given by

$$\Delta = \sum_\alpha e^{-\beta(U_\alpha + PV_\alpha)} . \qquad (23)$$

You should then be able to show that

$$G = -k_B T \ln \Delta(T, P, N) \qquad (24)$$

where $G = G(T, P, N)$ is the Gibbs potential, the Legendre transform of U with respect to S and V.

• <u>Summary</u>

The table below is a summary of essentially everything we've learnt so far about the basic structure of statistical mechanics. If there's one thing you should remember from this course, it is this table.

Macrostate	Partition Function	Definition	Thermodynamic connection	p_α
U,V,N	Microcanonical	$\Omega = e^{S/k_B}$	$S = k_B \ln \Omega$	$\dfrac{1}{\Omega}$
T,V,N	Canonical	$Q = \sum_\alpha e^{-\beta U_\alpha}$	$F = -k_B T \ln Q$	$\dfrac{e^{-\beta U_\alpha}}{Q}$
T,V,μ	Grand canonical	$\Xi = \sum_\alpha e^{-\beta(U_\alpha - \mu N_\alpha)}$	$\Psi = -k_B T \ln \Xi$	$\dfrac{e^{-\beta(U_\alpha - \mu N_\alpha)}}{\Xi}$
T,P,N	Isothermal-isobaric	$\Delta = \sum_\alpha e^{-\beta(U_\alpha + PV_\alpha)}$	$G = -k_B T \ln \Delta$	$\dfrac{e^{-\beta(U_\alpha + PV_\alpha)}}{\Delta}$

• Applications of the Canonical Formalism: The 2-State Model

As an illustration of how to apply the canonical formalism, consider a model system made up of N independent *distinguishable* particles, each of which can exist in only one of two possible energy states, one where its energy is 0 and the other where its energy is ε. This model is actually a variant of the model we began our study of statistical mechanics with – a gas whose individual particles could each be found in just two places: the left or right side of a closed container.

The gas in the earlier model was assumed to be isolated. But we'll assume that the present system is in contact with a heat bath, so that it's at a fixed temperature T. Our goal will be to calculate the system's canonical partition function, Q, and from there it's Helmholtz potential F, which governs all its thermodynamics. To do this, we need to identify the system's microstates, and the energies these microstates have. To get an idea of how to proceed, it helps to work first with a simple illustrative example: the case $N = 3$. For this example, there are $2^3 = 8$ microstates, which we list in the table below.

State label	Particle			U_α
(α)	1	2	3	
1	0	0	0	0
2	ε	0	0	ε
3	0	ε	0	ε
4	0	0	ε	ε
5	ε	ε	0	2ε
6	ε	0	ε	2ε
7	0	ε	ε	2ε
8	ε	ε	ε	3ε

With the energies of all the microstates in hand, we construct the Boltzmann factor $e^{-\beta U_\alpha}$ (also called the Boltzmann weight, or often just the weight) for each of the 8 microstates and then add them up. The sum by definition is Q, so

$$Q = e^{-\beta U_1} + e^{-\beta U_2} + e^{-\beta U_3} + e^{-\beta U_4} + e^{-\beta U_5} + e^{-\beta U_6} + e^{-\beta U_7} + e^{-\beta U_8}$$

$$= 1 + 3e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} \tag{25}$$

The structure of Eq. (25) suggests that it could just as well have been obtained by first summing up the Boltzmann weights for each *individual* particle, and then multiplying the results together. For a single particle, the energy states are 0 or ε, and so for the collection of 3 particles,

$$Q = (1 + e^{-\beta\varepsilon}) \times (1 + e^{-\beta\varepsilon}) \times (1 + e^{-\beta\varepsilon}) = (1 + e^{-\beta\varepsilon})^3$$

$$= 1 + 3e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

To calculate Q for the original N particle system, therefore, all we have to do is sum up the Boltzmann weights for each particle, and then multiply all the results together. In other words,

$$Q = \underbrace{(1 + e^{-\beta\varepsilon}) \times \cdots \times (1 + e^{-\beta\varepsilon})}_{N \text{ times}}$$

$$= (1 + e^{-\beta\varepsilon})^N \tag{26}$$

This is the result we were after, but it's important to note that we were able to obtain it so simply because the particles happened to be independent and distinguishable. This means that the same two energy states are accessible to each particle regardless of what states the other particles are in, allowing us to treat each particle separately.

Having found Q, we now use Eq. (8) to calculate F :

$$F = -Nk_BT \ln\left(1 + e^{-\beta\varepsilon}\right) \tag{27}$$

Other thermodynamic properties of the system – such as the constant volume heat capacity C_V, a readily measurable experimental quantity – can now be found. Consider C_V as an example; from its definition

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N} \tag{28}$$

we see that we need to evaluate a partial derivative involving the entropy. From the differential relation $dF = -SdT - PdV + \mu dN$, the entropy is given by

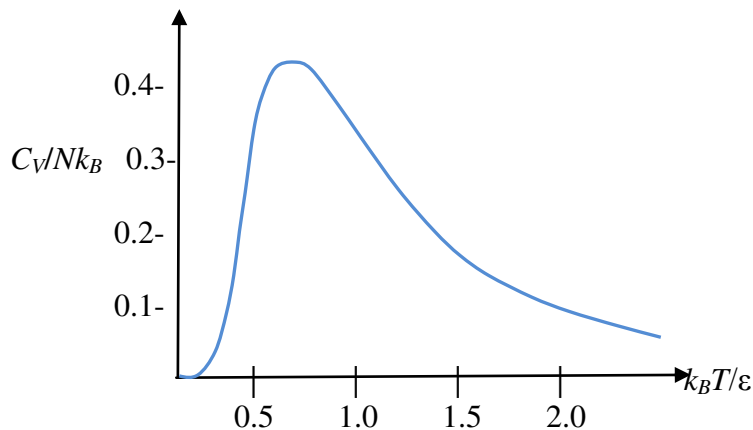$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \tag{29}$$

and so in terms of F,

$$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,N}, \tag{30}$$

which after introducing Eq. (27), becomes

$$C_V = Nk_BT\left(\frac{\partial^2}{\partial T^2}T\ln\left(1+e^{-\beta\varepsilon}\right)\right)_{V,N}$$

$$= N\frac{\varepsilon^2}{k_BT^2}\frac{e^{-\beta\varepsilon}}{\left(1+e^{-\beta\varepsilon}\right)^2} \tag{31}$$

A plot of C_V vs T as calculated from Eq. (31) looks roughly like this:

The shape of this curve is actually characteristic of a number of materials in which the two lowest lying energy states lie far below the next higher energy states, and the maximum is often referred to as a "Schottky hump".

So the two-state model is not as artificial as it might seem! And it happens to be a great paradigm for a number of biological processes, as we'll soon see. But before getting to those processes, we need to recognize that the calculation of the canonical partition function Q can be carried out both as a sum over states and as a sum over "levels". This point is elaborated on in the next section.